

Carbon confined GeO₂ hollow spheres for stable rechargeable Na⁺ batteries

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Experimental Section

Materials.

Ar was supplied by Longhai Factory with a purity of 99.999%. Vinyl imidazole, divinylbenzene (DVB) and dibromobutane were purchased from J&K. Initiator 2, 2-azobisisobutyronitrile (AIBN) was purchased from Aladdin. Other chemicals and solvents were obtained from local suppliers. The water used in all experiments was supplied by ultrapure water purification system.

Preparation of ionic liquid monomer 1,4-butyl-3,3'-divinylimidazolium dibromide [BDVIm] Br₂.

Vinyl imidazole (9.41 g, 100 mmol) and 1,4-dibromobutane (10.80 g, 50 mmol) were dissolved in chloroform (100 mL) in a 250-mL round-bottomed flask. The mixture was stirred at reflux for 24h. After reaction, the top phase was removed, and the oily residue was washed three times with chloroform, then dried under reduced pressure to remove residual chloroform. White powder (19.81 g) was obtained in a yield of 98 %.

Preparation of GeO₂@C

[BDVIm] Br₂ (1.50 g) and GeCl₄ (1.00 g) was dissolved in 10 mL ethanol in a 100-mL round-bottom flask and stirred at room temperature for 2 h. Then AIBN (0.25 g) was added and the polymerization reaction was conducted at 75 °C for 12 h. When cooling to ambient temperature, excess amount of water was added immediately to insure fully hydrolysis of Ge⁴⁺. After washed with deionized water three times and dried overnight, the PIL supported GeO₂ nanoparticles (GeO₂@PIL) was obtained. Under the Ar atmosphere at 500 °C, GeO₂@PIL was carbonized for 10 h to obtain the nitrogen doped carbon confined GeO₂ nanostructures (GeO₂@C).

Characterizations

The phase structure of samples was determined by a powder X-ray Diffractometer (Bruker D8, Cu K α radiation, $\lambda = 1.5406 \text{ \AA}$, voltage: 40 kV, current: 40 mA) at a scan rate of 6° min^{-1} between 10° and 90° . The morphology of the samples was investigated by employing a Field-emission scanning electron microscope (FESEM, Thermo Fisher, Varios G4 UC). The microstructures of the samples were further detected on Transmission electron microscope (TEM, Tecnai G2 F20) and high-resolution transmission electron microscopy (HRTEM) by directly dripping them on a copper grid. The elemental maps were obtained using the SEM energy dispersive spectrum (EDS). X-ray Photoelectron Spectra (XPS) were recorded by an X-ray photoelectron spectroscopy (Thermo Fisher K-Alpha USA).

Electrochemical performance

The GeO₂@C sample powders were mixed with a binder (poly(vinylidene fluoride), PVDF) and acetylene black with a weight ratio of 8: 1: 1 to obtain a mixture slurry by dissolving in N-methyl-2-pyrrolidone (NMP) solution. The mixed slurry was uniformly coated on a copper substrate (14 mm in diameter) with a mass loading of $\sim 10 \text{ mg}$. Square sodium foils with side length of $\sim 12 \text{ mm}$ were made from bulk-sodium (Aladdin, 99.9%) in an Ar gas filled glove box. The electrolyte of NIBs is 1.0 M NaClO₄ solution (the volume ration of dimethyl carbonate (DMC), ethylene carbonate (EC) and fluoroethylene carbonate (FEC) is 10: 10: 1), while the electrolyte of LIBs is 1.0 M LiPF₆ solution (the volume ration of ethylene carbonate (EC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC) is 1: 1: 1). Polypropylene glass microfiber filters (Whatman GF/D) and polypropylene (PP) film (Celgard 2500) were used as separators of NIBs and LIBs, respectively. To evaluate the electrochemical performance of the prepared samples, coin cells (CR2032-type for NIBs and CR2016-type for LIBs) were assembled in an argon-filled glove box. Cyclic voltammetric (CV) tests were performed on an electrochemical workstation (Zennium, IM6, Germany) with a scan rate of 0.10 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) tests were conducted in the frequency window between 100 kHz and 100 mHz at (5 mV). The galvanostatically charge/discharge and rate tests of coin-type cells were cycled on a LAND CT 2001A instrument (Wuhan, China) at room temperature. The voltage window for all tests is 0.01–3.0 V.

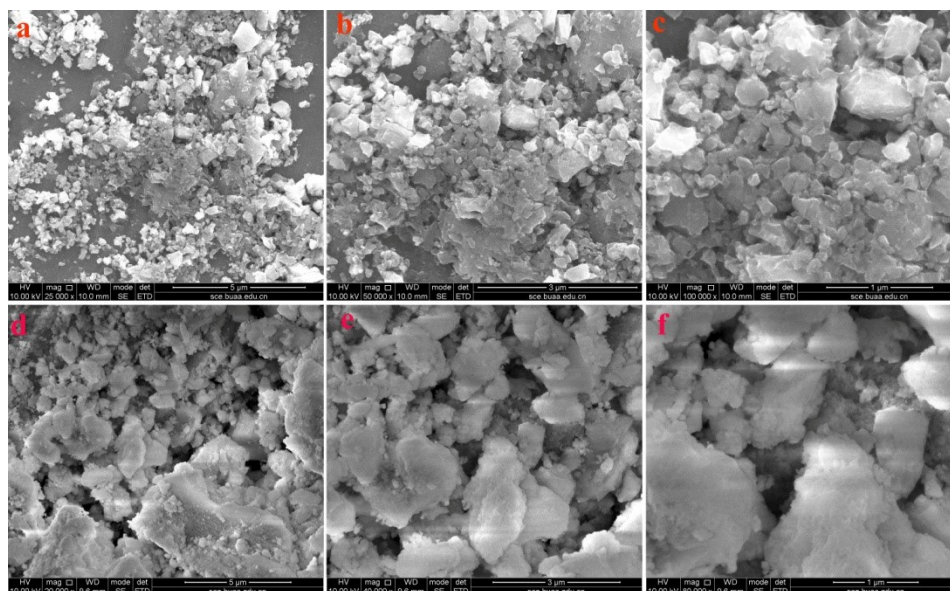


Figure S1. SEM images of (a-c) pure C obtained at the absence of Ge precursor and (d-f) commercial GeO₂ powders at different magnification.

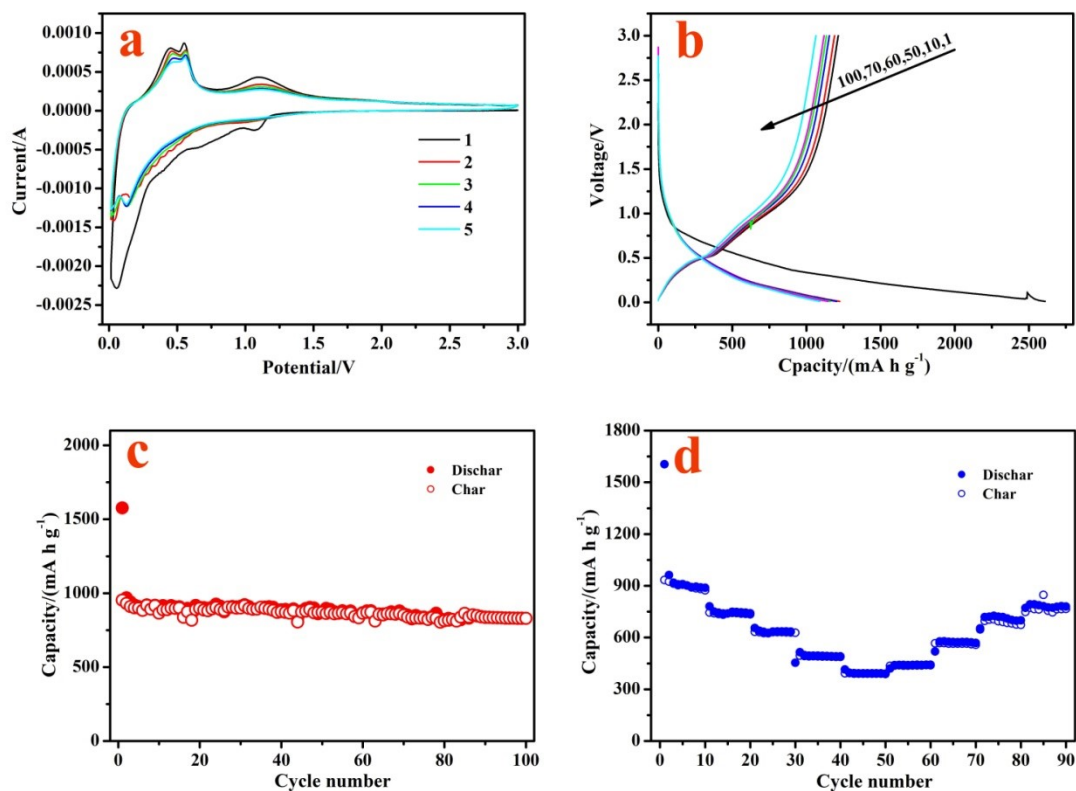


Figure S2. Li storage performance of the Ge@C electrode. (a) Cyclic voltammograms for 1 ~ 5 cycles at a scanning rate of 0.1 mV s⁻¹; (b) Charge/discharge- profiles for selected cycles under the current density of 200 mA g⁻¹; (c) Cycling performance under the current density of 200 mA g⁻¹; (d) Rate performance of the Ge@C electrode.

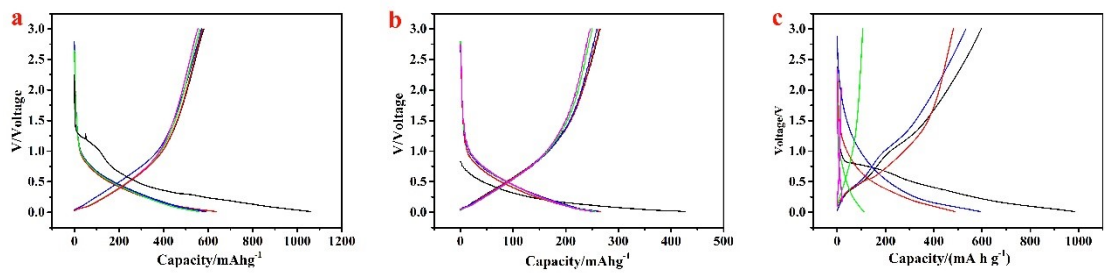


Figure S3. The discharge-charge curves of the (a) $\text{GeO}_2@\text{C}$, (b) pure C, and (c) GeO_2 electrodes at 1st, 2nd, 3rd, 50th and 100th cycles.

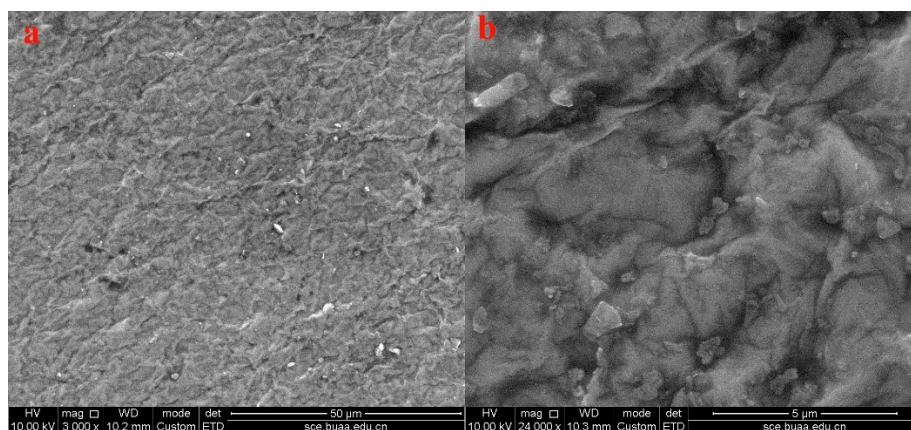


Figure S4. The surface morphology of $\text{GeO}_2@\text{C}$ electrode after 500 cycles, from which it can be found that the electrode could maintain integrity after long charge-discharge cycles.